Photodarkening effects in semiconductor-doped glasses

B. Van Wonterghem, S. M. Saltiel,[a] T. E. Dutton, and P. M. Rentzepis
Department of Chemistry and Physics, University of California, Irvine, California 92717

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The fading of the phase conjugation efficiency and luminescence quantum yield in CdS_xSe_{1-x}-doped glasses was investigated as a function of laser exposure using pulsed and cw mode-locked lasers. An analysis of the kinetics of the photodarkening effect is presented. The rate constant of the fading process depends nonlinearly upon the laser fluence and is sensitive to the origin of the glass.

INTRODUCTION

Semiconductor CdS_xSe_{1-x}-doped glasses are interesting composite materials for several reasons. First, they have large nonlinear optical susceptibilities,[1-3] a picosecond response time at high excitation intensities,[4,5] and they are promising materials for the construction of all-optical switching devices.[6] Second, the size of the semiconductor microcrystals ranges from 60 to 100 Å, and the carrier motion is confined in three dimensions; so this kind of material can be used to study quantum size effects. Many efforts have been exerted to observe these effects at room temperature in commercially available glasses, but due to the broad size distribution of the semiconductor microcrystals, no characteristic structure in the optical absorption edge and the luminescence spectra has been detected. For the study of the quantum size effect,[7-9] better control of the microcrystalline sizes and distribution is required, as has been realized in laboratory prepared glasses. Several groups[2,4,5,10-12] noticed a modification of the optical properties of CdS_xSe_{1-x}-doped glasses upon exposure of the sample to laser beams during their experiments. Roussignol *et al.*[2,10] called this effect "darkening" because of the observed small change of the sample absorption. They observed a decrease of the phase conjugation efficiency by a factor of 2 when exposing the glass to 15 J/cm^2 with single picosecond pulses, each having a fluence of 5 mJ/cm^2. An even larger reduction of the luminescence efficiency was also reported. The same authors argue that no change in the sample is observed when the fluence is less than 0.5 mJ/cm^2. An important advantage of this modification of the sample is that the decay time of the nonlinear response decreases by one to two orders of magnitude. For example, in an exposed OG530 color filter, a response time as short as 50 ps was observed, which is 200 times shorter than in an unexposed spot.[2] A carrier recombination time of 7 ps has been observed in a Hoya semiconductor-doped glass after being exposed for 3 h.[4]

The luminescence spectrum of semiconductor CdS_xSe_{1-x}-doped glasses usually consists of two bands, one assigned to direct carrier recombination and the other red shifted relative to the band gap, is due to trapped carrier recombination. The broad emission band attributed to trap recombination almost completely disappears upon prolonged laser exposure.[2] The exposure-modified spots were found to be stable at room temperature. However, heating of a photodarkened glass at 400 °C for 4 h eliminates the changes and restores the original optical properties.[2,5]

Photodarkening effects obviously complicate optical measurements on these glasses especially when using high-power laser sources. This is one of the reasons for the large discrepancy in the published data on the third-order nonlinear susceptibility $\chi^{(3)}$, whose value varies by about four orders of magnitude.[11] Tomita, Matsumoto, and Matsuoka,[13] suggested that the photodarkening effect is significantly reduced at low temperatures, and for this reason they performed all their experiments concerned with nonlinear optical properties of semiconductor-doped glasses at liquid-nitrogen temperature. As will be described later, our experimental data on Schott OG550 glass are in contradiction with this statement.

A recent review by Williams *et al.*[6] states that the exact cause of the elimination of trapped carrier recombination in CdS_xSe_{1-x}-doped glasses is not well understood and that more experiments are needed in order to develop a model which explains the photochemical changes in such composite materials. The results reported in Refs. 2, 4, and 5 refer only to high-power experiments. Here we report a study of the photodarkening effects in semiconductor CdS_xSe_{1-x}-doped glasses by following the phase conjugation and luminescence efficiency as a function of the exposure history of the sample. We show that even a fluence as small as 10 nJ/cm^2 causes a significant photodarkening effect. Our experimental data suggest that there is no threshold for the photodarkening effect; however, we find a nonlinear dependence of the photodarkening rate constant on peak power.

EXPERIMENTAL RESULTS

Most of the experiments have been performed with a frequency-doubled cw mode-locked Nd:YAG laser (average output power, 1 W; pulse duration, 70 ps; repetition rate, 80.5 MHz). The experimental setup, shown in Fig. 1, allows for simultaneous measurement of phase conjugate reflectivity and luminescence efficiency. All beams were vertically polarized and had a $1/e$ radius of 1 mm in the sample. A retroreflection configuration was used for generation of the phase conjugate beam by degenerate four-wave mixing.[14] The phase conjugate intensity was recorded by a lock-in amplifier (LOCK-IN 2) locked to the difference frequency of the pump and probe beam chopping frequencies, while the luminescence signal was recorded by a lock-in amplifier

[a] Permanent address: Department of Physics, Sofia University, Sofia 1126, Bulgaria.

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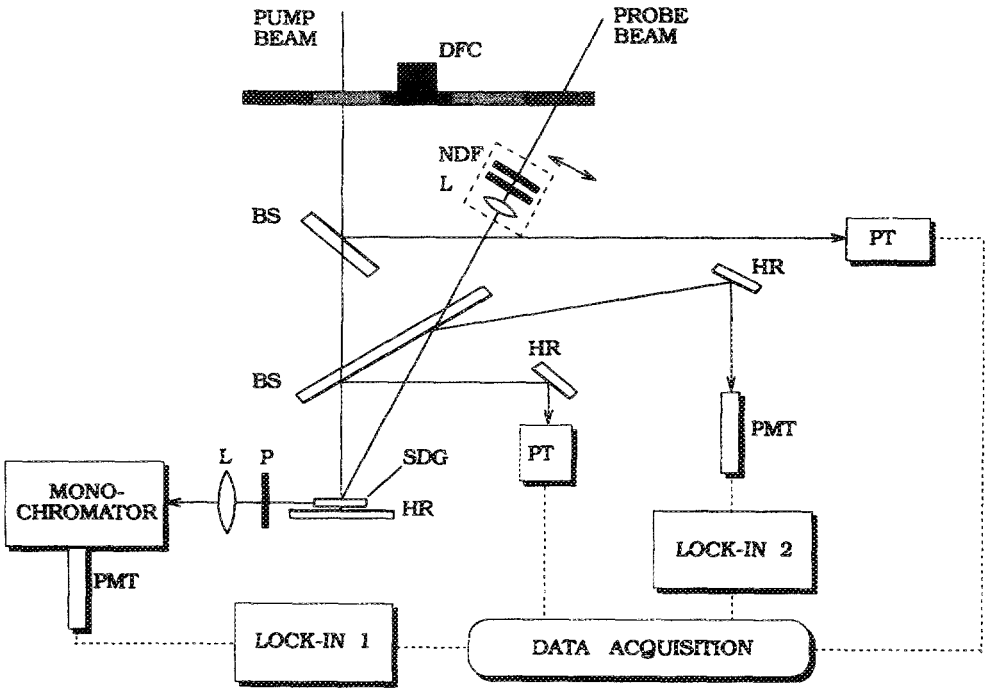

FIG. 1. Experimental system used for measurement of fading of phase conjugation and luminescence efficiency. DFC: dual frequency optical chopper; NDF: neutral density filters; L: lens; BS: beam splitter; HR: high reflecting mirror; SDG: semiconductor-doped glass; P: polarizer; PT: phototube; PMT: photomultiplier.

(LOCK-IN 1), triggered by the probe beam chopper frequency. All luminescence intensity measurements were recorded at the maximum of the trap emission band (740 nm). This setup is a modification of the experimental system described earlier in Ref. 14. The pump intensities in most of the experiments were less than 3 kW/cm^2, far below the level where saturation of the phase conjugation efficiency becomes noticeable.[1,2,11] We performed a similar experiment for the measurement of the luminescence efficiency saturation (Fig. 2). Below 1 kW/cm^2 the decrease in luminescence efficiency with the increasing pump power is relatively small, and the luminescence efficiency may be considered as constant.

High-power experiments were performed using a pulsed mode-locked Nd:YAG laser (maximum energy, 2 mJ/pulse, at 532 nm; rep. rate, 2 Hz and 25-ps pulse width). This setup used counterpropagating pump beams to generate four-wave mixing as described in Ref. 15. Experiments were performed on Corning filter 3-68 and Schott filter OG530, both $CdS_{0.9}Se_{0.1}$-doped glasses. Their thickness was 3 mm, and the transmission at 532 nm was 0.25 and 0.50, respectively. A Schott glass OG550 with room-temperature transmission of 0.01 was used in the liquid-nitrogen experiments.

Initially, some experiments were performed on semiconductor-doped glasses at very low temperatures to verify the statement that photodarkening would be negligible at liquid-nitrogen temperature.[13] Due to the strong temperature dependence of the band gap in CdS_xSe_{1-x}, the transmission of the OG550 glass at 532 nm increased from 0.01 at room temperature to 0.42 at -196 °C. At this temperature the trap luminescence increased and also underwent a blue shift. The fading of the luminescence efficiency with laser exposure at room and liquid-nitrogen temperature are shown in Fig. 3. The mean power of the beam used for exposure was 140 mW, while the luminescence efficiency was

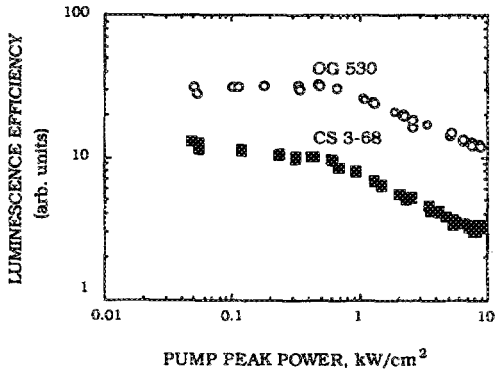

FIG. 2. Measured luminescence efficiency as a function of pump peak power: O: Schott OG530 color glass filter; ■: Corning 3-68 color glass filter.

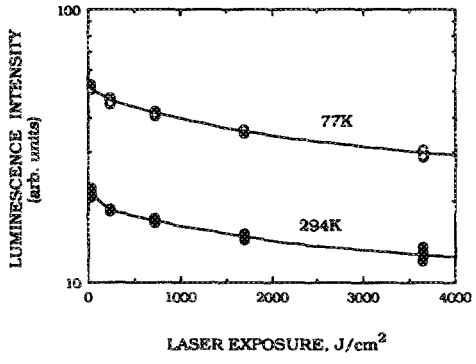

FIG 3. Fading of luminescence efficiency with laser exposure at room (●) and liquid-nitrogen (O) temperature in OG550 filter. The solid lines are intended to guide the eye.

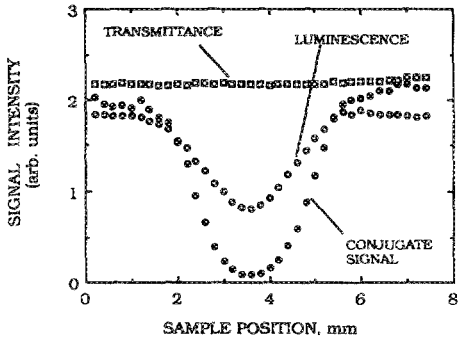

FIG. 4. Radial profile of the transmission (□) at 532 nm, the phase conjugate reflectivity (●), and luminescence efficiency (○) of a "dark" spot in Corning 3-68 filter.

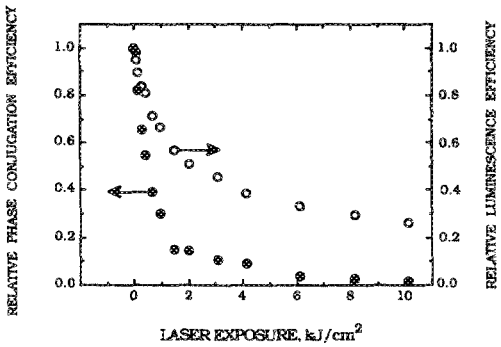

FIG. 5. Phase conjugation (●) and luminescence (○) efficiency as a function of laser exposure for Corning 3-68 filter.

probed by the same beam, attenuated 100 times in order to avoid exposure effects during the measurement. We observed a similar luminescence decrease at both temperatures. Since this glass absorbs 40% less light at −196 °C than at room temperature, the photodarkening effect is even stronger at liquid-nitrogen temperature, at least for the Schott semiconductor-doped glasses studied. Subsequently, all other measurements have been performed at room temperature.

On continued exposure the phase conjugation and luminescence efficiencies decrease and reach a constant level, which depends on the nature of the sample and the applied exposure fluence. Figure 4 shows a radial profile of the transmission at 532 nm, the phase conjugate reflectivity, and luminescence efficiency of a "dark" spot, created by exposing a Corning 3-68 for more than 10 h to a 130-mW laser beam. The experiments were performed by scanning the exposed spot using very low-power probe beams (less than 5 mW). Note that the transmission of the glass is hardly changed by this exposure. For this reason the exposed areas cannot be recognized visually, but can be detected easily by illuminating the glass with a diffused 532-nm laser beam and observing the luminescence of the sample through an orange filter. Exposed areas will appear as dark holes in the luminescent glass. In contrast to the low-peak-power exposure experiments discussed above,the modified spots created by exposure to high-energy pulses of a pulsed mode-locked Nd:YAG laser cause a visible change in transmission.

As illustrated in Fig. 4, the photodarkening effects are spatially inhomogeneous, due to the Gaussian intensity profile of the pump beam, causing a faster fading of the phase conjugation and luminescence efficiency in the center of the beam than at its boundary. To correct for these effects on the determination of fading rate constants, the luminescence and phase conjugation efficiency were measured in the center of the exposed spot by focusing the probe beam through a 1-m focal-length lens and attenuating its intensity by a factor 20. The experimental procedure consisted of exposing the sample for various time intervals and probing the sample between exposures, using a 40-times attenuated pump beam and a very low-power probe beam, to avoid darkening effects during the measuring interval. A simultaneous recording of phase conjugation and luminescence efficiency of a Schott OG530 glass as a function of exposure is shown in Fig. 5. The sum of the power of the pump and probe beams was 130 mW. The decrease of the phase conjugation efficiency is considerably larger than the decrease of the luminescence efficiency. We also compared luminescence spectra in a "fresh" and a "dark" (long-time-exposed) spot. The intensity of the broad trap recombination band decreases as compared to the direct radiative recombination band (as noted in Ref. 2), but no changes in the peak wavelength of the trap emission band or in its shape were noticed.

We investigated further the influence of peak power on the photodarkening effect using the high-energy pulses of a pulsed mode-locked Nd:YAG laser. In Fig. 6 we compare the decay of the phase conjugate signal on exposing the sample to the 532-nm output of a cw mode-locked Nd:YAG laser and a pulsed mode-locked Nd:YAG laser. The decay rate is higher when the sample is exposed to high-peak-power pulses. The absolute decrease of phase conjugation efficiency at high peak power is smaller when compared to the decrease in the low-power phase conjugation measurements. This observation can be explained by the fact that at high peak powers the phase conjugation is not entirely due to traps, but also to band-gap-related phenomena.

DISCUSSION

To explain our experimental results, we performed a kinetic analysis of the fading using a simplified model for the

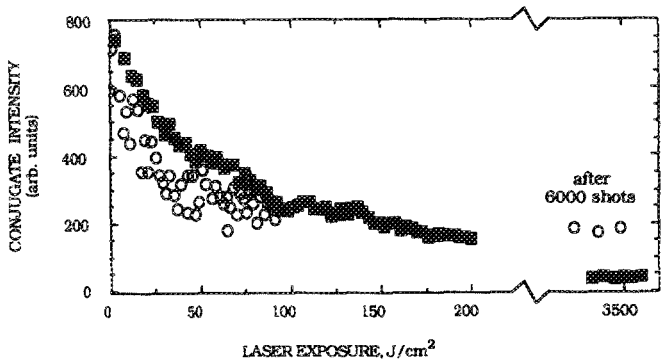

FIG. 6. Dependence of phase conjugate signal in OG530 on exposure of the sample to the 532-nm output of a cw mode-locked Nd:YAG laser with total power of 130 mW (■) and a pulsed mode-locked Nd:YAG laser, 2 mJ per shot (○).

energy levels involved in the deep trap radiative recombination and phase conjugation. At high peak powers the phase conjugate reflectivity is partly due to traps and partly to band-gap-related nonlinear processes such as band filling and electron-hole plasma formation. At low pump powers, the phase conjugation is mainly due to the creation of a population grating of long-lived trapped carriers[16] in the semiconductor microcrystals. An argument confirming this mechanism is the fact that we observe similar lifetimes for the phase conjugation and trap luminescence decays, ranging from 5 to 20 μs in OG530 and CS 3-68 glasses. These results will be published elsewhere. The long-lived grating is often explained by thermal effects, but as it has been shown by Eichler for pure CdS, these microsecond grating decay times are independent of the grating spacing and therefore cannot be explained by diffusive decay mechanisms.[17] Recent experiments in semiconductor-doped glasses,[16] where the angle between pump and probe beam was varied, also confirmed that thermal effects are small.

The similarity of the fading of the phase conjugation and trap-recombination luminescence efficiency, and the fact that the trap luminescence spectrum remains unchanged under irradiation, suggests the following model to explain our results. (a) The same trap level T (or group of levels) is responsible for the luminescence and phase conjugation process. (b) The number and properties of the traps T remain unchanged under irradiation. (c) Under the influence of laser exposure, a different kind of trap, Q is created, opening an additional channel for radiationless recombination of the excited carriers. This process decreases the population of level T and consequently of the phase conjugation and luminescence efficiency. The proposed energy-level diagram is shown in Fig. 7. It consists of valence band V, conduction band C, and two types of deep trap levels, T and Q. Excited carriers in the conduction band will either undergo direct recombination, responsible for the high-energy luminescence band, or will populate trap levels T and Q with rates $k_{C,T}$ and $K_{C,Q}$, respectively. We assume that initally only trap sites of the kind T are present in the semiconductor microcrystallites. The trapping rate $k_{C,Q}$ at the radiationless recombination sites Q is proportional to the number concentration of the sites [Q], which increases in the sample as a function of laser exposure:

$$k_{C,Q} = k^*_{C,Q}[Q] = k^*_{C,Q} k_Q \beta,$$

where $k^*_{C,Q}$ is the trapping rate constant for Q and k_Q is the creation rate of the recombination centers under the influence of the exposure β. The recombination rate via traps T and Q are denoted as $k_{T,V}$ and $k_{Q,V}$. The rate equations for this energy-level diagram are

$$\frac{dN_C}{dt} = \frac{I\sigma_0 N_V}{h\nu} - (k_{C,T} + k_{C,Q} + k_{C,V})N_C,$$

$$\frac{dN_T}{dt} = k_{C,T}N_C - k_{T,V}N_T,$$

$$\frac{dN_Q}{dt} = k_{C,Q}N_C - k_{Q,V}N_Q, \tag{1}$$

where the population of the carriers in V, C, T, and Q levels are denoted as N_V, N_C, N_T, and N_Q, respectively. $N_0 = N_V + N_C + N_T + N_Q$. I is the pump intensity. σ_0 is the absorption cross section for e-h pair creation.

In the case of weak excitation the contribution of direct band-gap recombination is relatively small and the term $k_{C,V}N_C$ can be neglected. The steady-state solution for N_T, the population of the level, which we probe by measuring luminescence and phase conjugation efficiency, is

$$N_T = \frac{I\sigma_0 N_0}{h\nu} \frac{k_{C,T}}{k_{T,V}(k_{C,T} + K_{C,Q})}. \tag{2}$$

The luminescence signal is proportional to N_T, while the conjugate signal is proportional to N_T^2 (see, for example, Ref. 18). Therefore,

$$\frac{I_{lum}(\beta = 0)}{I_{lum}(\beta)} = 1 + k_{lum}\beta,$$

and

$$\frac{I_{conj}(\beta = 0)}{I_{conj}(\beta)} = (1 + k_{conj}\beta)^2, \tag{3}$$

where $k_{lum} = k_{conj} = k^*_{C,Q}k_Q/k_{C,T}$.

According to this model the ratio of the luminescence from a "fresh" spot to the luminescence from an exposed spot should be proportional to the exposure β. The same is true for the square root of the phase conjugate signal. The reciprocal values of k_{lum} and k_{conj} are equal to the exposure needed for reducing the luminescence intensity twice, and phase conjugation efficiency four times, respectively.

For the experimental verification of expression (3), we used the data presented in Fig. 5. In Fig. 8(a), we plot the ratio

$$I_{lum}(\beta = 0)/[I_{lum}(\beta) - I_{lum}(\beta = \infty)]$$

as a function of β. In the same way for the phase conjugate signal, we show in Fig. 8(b) the dependence of

$$I^{1/2}_{conj}(\beta = 0)/[I^{1/2}_{conj}(\beta) - I^{1/2}_{conj}(\beta = \infty)]$$

on the exposure β. Figures 8(a) and 8(b) indicate that there is a good agreement with the proposed model for the photokinetics of the darkening process. From the data in Fig. 8, we obtained a rate constant $k_{lum} = 0.60 \pm 0.10$ cm^2/kJ for the luminescence intensity fading and $k_{conj} = 0.65 \pm 0.05$ cm^2/kJ for the phase conjugation efficiency decrease. A similar analysis for the Schott OG530 glass yielded the following rate constants: $k_{lum} = 5.45 \pm 0.2$ cm^2/kJ and $k_{conj} = 5.2 \pm 0.6$ cm^2/kJ. These values were obtained

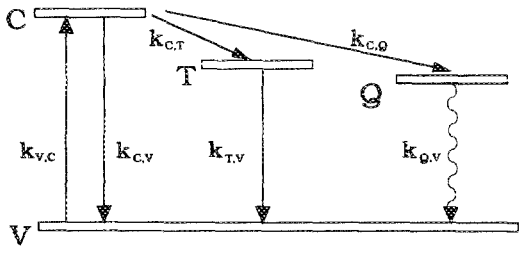

FIG. 7. Energy levels participating in the photodarkening process of semiconductor-doped glasses. V: valence band; C: conduction band; T and Q: trap levels.

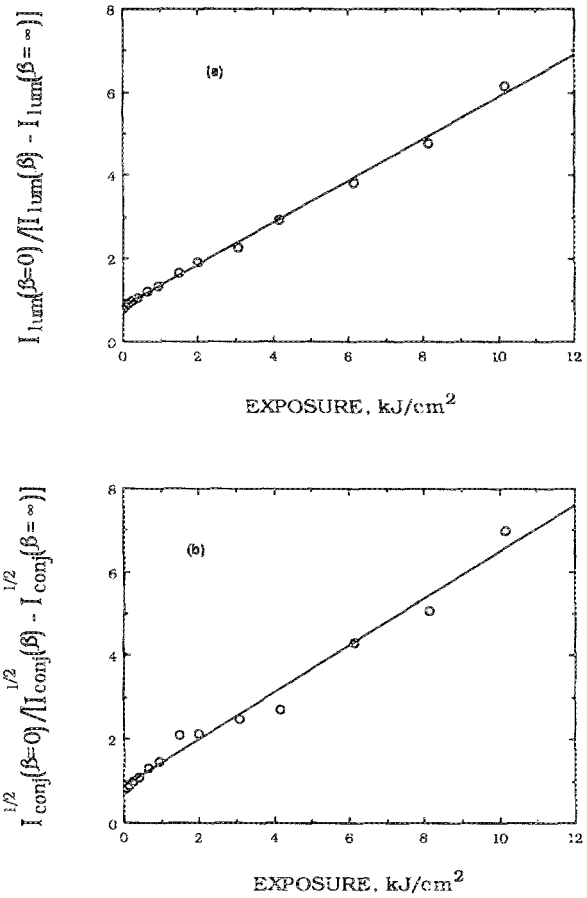

FIG. 8. Plot of (a) reciprocal normalized values of the luminescence intensity and (b) the square root of the conjugate signal as a function of exposure. The lines are fit to the theoretical expressions (3).

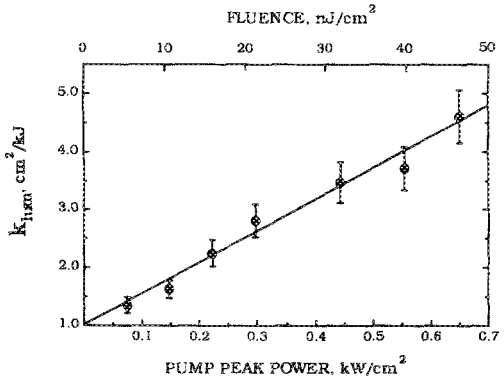

FIG. 9. Luminescence fading constant as a function of the peak power of the exposing beam. Each measurement is taken at a new nonexposed place of the OG530 filter.

with 1 kW/cm^2 peak power in the exposing beam. The experimental rate constants for phase conjugation and luminescence fading can be considered equal within experimental error, indicating that the nonlinear refractive index change originates in the same kind of recombination centers that is responsible for the red-shifted luminescence. The Corning semiconductor-doped glasses are almost one order of magnitude more resistant to exposure than the glasses produced by Schott.

An important question, in resolving the mechanism responsible for this darkening effect, is how these rate constants depend upon the fluence of the pump beam. The results shown in Fig. 9 were obtained by varying the peak power of the pump beam using an attenuator which consist half-wave plate and polarizer, and increasing the exposure time proportionally to keep the total light dose constant. These results clearly indicate a faster photodarkening effect with increasing intensity of the pump beam. Similar results have been observed for the trap recombination luminescence fading, but at higher pump intensities (10^5–10^6 W/cm^2).[5] From data published in Refs. 2 and 5 we calculated the following fading rate constants: $k_{lum} = 1.66$ cm^2/kJ for Corning 258 filter at 1 MW/cm^2 pump power and $k_{conj} = 27$ cm^2/kJ for Schott OG570 filter at 0.5 MW/cm^2. It is important to note that at this high-power level the traps are almost completely saturated, causing the fading rate to be independent of the intensity.

In terms of the suggested model, the data presented in Fig. 9 indicate that the coefficient $k_{lum} = (k^*_{C,Q}/k_{C,T})k_Q$ increases with increasing pump intensity. Several factors can be responsible for this effect. Local temperature changes in the semiconductor microcrystals due to pump beam absorption influence the carrier mobility and the various rate constants involved in the decay process, leading to increase in the rate constant k_Q. In Ref. 16, it is suggested that the decrease in the population of level T can be attributed to trap photoionization taking place at higher intensities.

CONCLUSION

We have described the fading mechanism of the phase conjugation and luminescence efficiency in semiconductor-doped glasses as a function of laser-exposure history of the sample. The "darkening effect" is stronger in the Schott glasses than the equivalent glasses produced by Corning. It is shown that the low-power phase conjugation and luminescence process are due to the same group of trap levels. Based on our results and previously published data, the main consequences of the darkening process are an irreversible (at room temperature) decrease of phase conjugation and luminescence efficiency to a fraction of its original level and a shortening of the decay time of the nonlinearly induced index change and luminescence. The darkening proceeds faster at higher intensities.

The results reported here show that the photodarkening induces a significant change in the (nonlinear) optical properties of semiconductor-doped glasses and therefore ought to be taken into account when working with this kind of materials and comparing results obtained by different groups.

ACKNOWLEDGMENTS

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